NCCAVS Annual Symposium
February 22, 2018

Thin film roadmap for solid state Li Metal Batteries

Ernest Demaray – Published Thin Film Patent

Pavel Khokhlov – Design, Fabrication and Test

Aubert Demaray- Market Applications

Outline

- **Patent application "Thin film Battery with High Capacity, energy Density and Cycle life" published US20180006293A1 January 4, 2018.**
- **AVS 2017 - SpectraPower/DLLC demonstrated Hybrid Lithium metal cells with capacities of 500 Whr/kg but with limited cycle life.**
- **AVS 2018 - SpectraPower/DLLC Lithium metal test cells have demonstrated improved cycle life while keeping the same energy density.**
- **2012-2018 Solid-state all thin film Li metal cells (<1mAhr) are in large scale commercial production today using DLLC patented process and reactor technology with 4,000 cycle life (STMicro) and 10,000-60,000 cycle life demonstrated ORNL .**
- **Technology development is in progress targeting high capacity volume production in the future.**
- **SpectraPower/ DLLC hybrid Lithium metal cells using 300mm semiconductor sputtering hybrid with SpectraPower's high capacity NMC cathode, design, assembly, test show commercial feasibility for pilot/prototype cells 2017-'18.**
- **Many high value market applications are available for early applications of cells for batteries with 2-3 X higher energy density than Li+ ion cells.**

Hybrid Thin Film Battery Patent Published

Patent for hybrid battery with
High capacity NMC cathode (14,15)
And thin film anode (10, 11,12) and
solid state electrolyte (13)
published Jan. 4, 2018.

Go to **www.pat2pdf.com**
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US 20180006293A1

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(12) **Patent Application Publication** (10) **Pub. No.: US 2018/0006293 A1**
DEMARAY et al. (43) **Pub. Date: Jan. 4, 2018**

(54) **THIN FILM BATTERY WITH HIGH CAPACITY, ENERGY DENSITY AND CYCLE LIFE**

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(73) Assignee: **DEMARAY, LLC**

(21) Appl. No.: **15/590,887**

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Related U.S. Application Data

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Publication Classification

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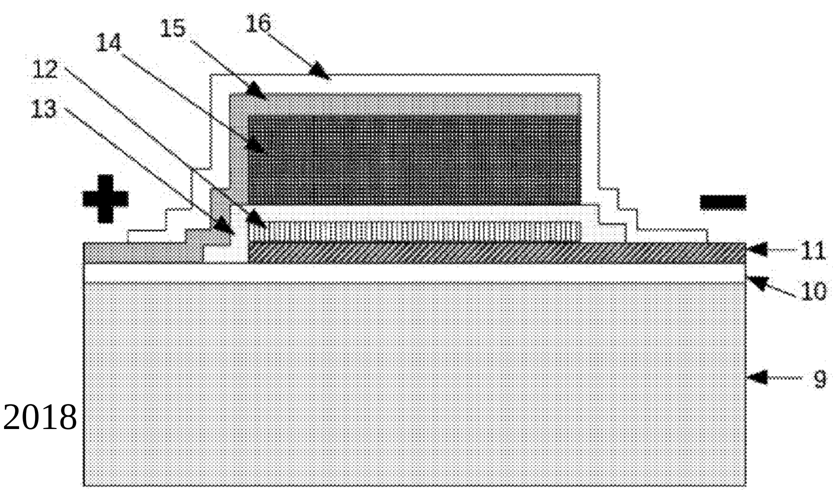
C01G 23/00 (2006.01)
H01M 4/64 (2006.01)

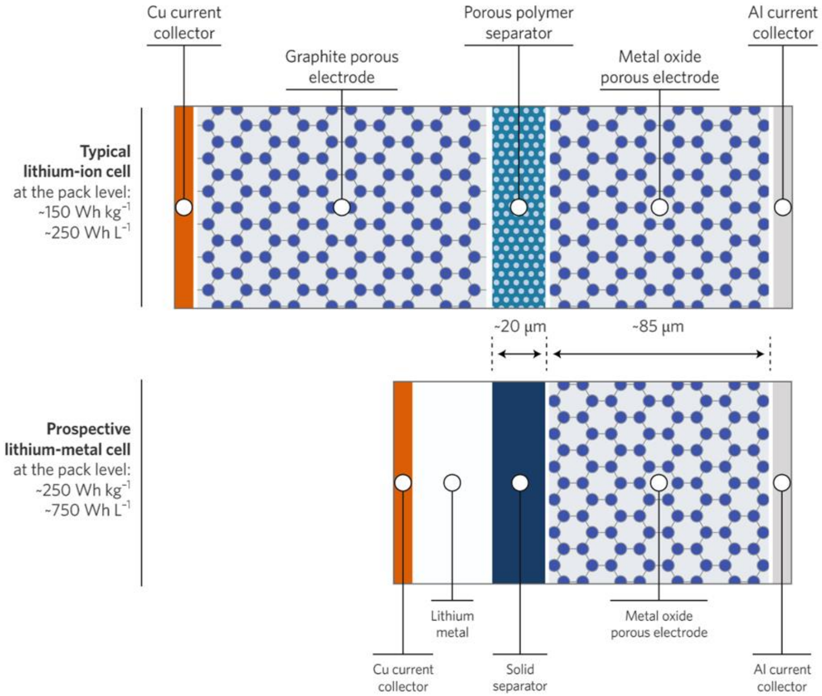
(52) **U.S. Cl.**
CPC *H01M 4/0423* (2013.01); *H01M 4/64* (2013.01); *C01G 23/00* (2013.01); *H01M 4/0404* (2013.01)

(57) **ABSTRACT**

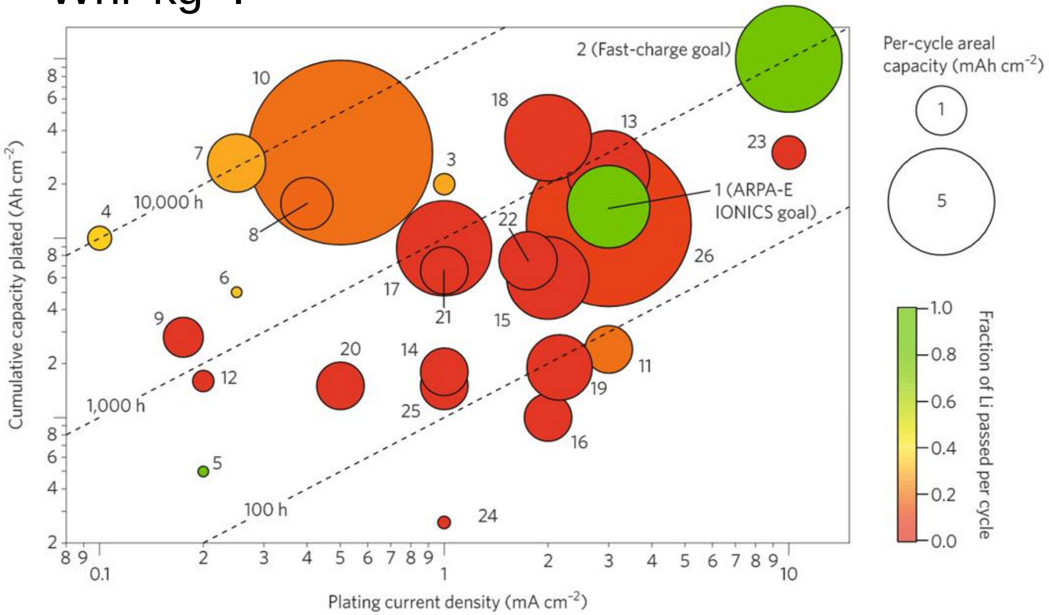
Embodiments of the present invention are in the field of materials, apparatus, process, methods, and designs for manufacture of a thin film energy storage devices with a capacity greater then 1 mA-hr-cm^{-2} including thin film Lithium metal and Li+ ion batteries and capacitors having high energy density and high cycle life due to the incorporation of at least one vacuum thin film with respect to protection and electrical conductivity of the electrodes, and at least one vacuum thin film electrolyte for electrical insulation of the electrodes and ion conduction after assembly for low self discharge and high cycle life battery cells.



DOE forecast for Li metal cell energy density improvement over Li+ ion cell



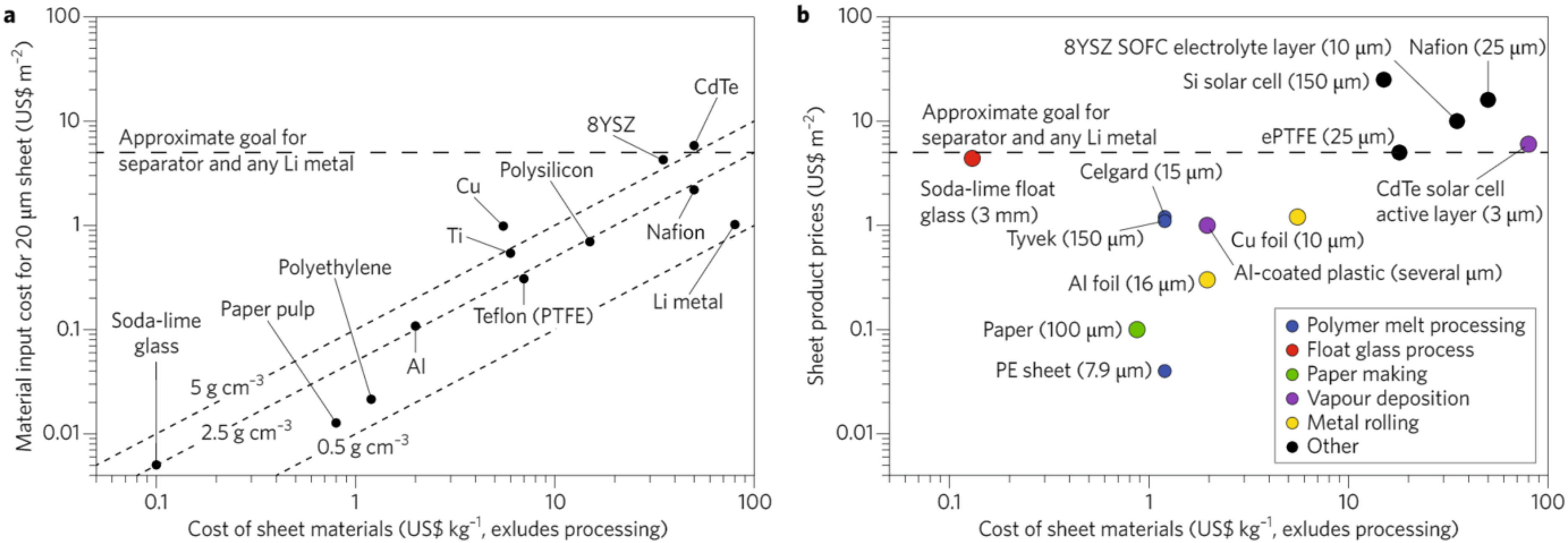
DOE shows the benefit over Li+ ion cell volume for ~ 30 microns of Li metal which could lead to ~ 300Whr/kg. Thin film anode alone is shown below to achieve 500-750 Whr-kg^{-1}.



Paul Albertus, et. al., Status and challenges enabling Lithium metal .. batteries, Nature Energy, V.3, Jan. 2018, pp16-21

DOE cell with 30 microns Li metal achieves ~ 4.8 mAh/cm2 not 8mAh/cm2 As demonstrate by SpectraPower/DLLC In 2017.

DOE forecast for Li metal cost improvement over Li+ ion

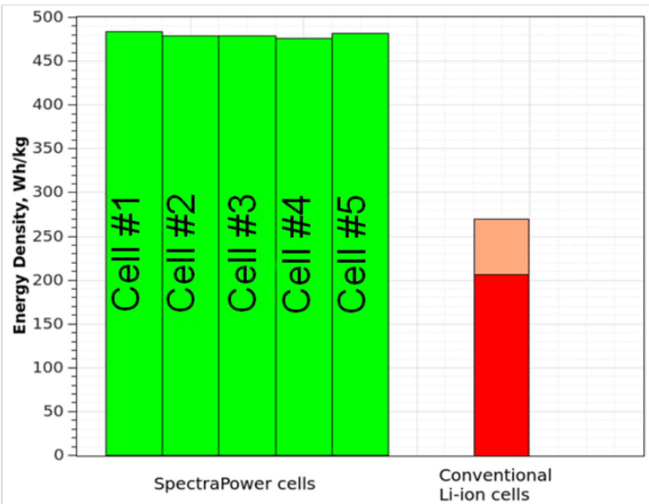


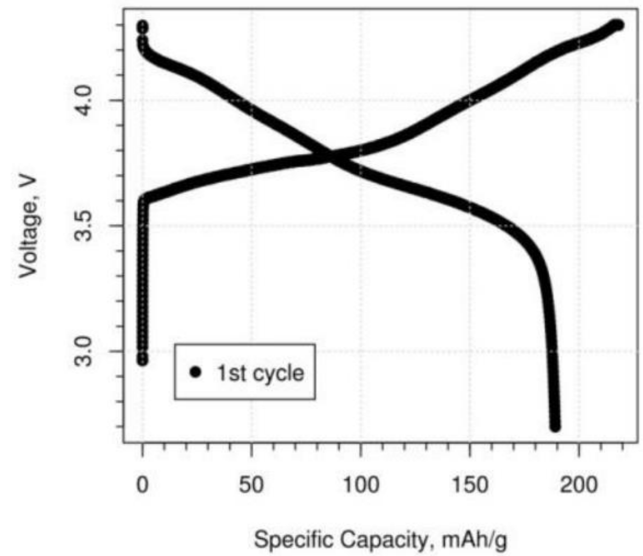
By adhering to traditional bulk material fabrication methods with ~ 20 micron thick battery layers, DOE/ARPAe energy density is limited and material costs are high.

Referencing the cost of CdTe as ! $100/kg as representative of thin film materials is disingenuous and misleading. Production thin film costs with inline sputtering are on the order of $15/micron-meter^2, well within the reach of affordable cell production.

Ultra-High Energy Density Rechargeable Li-metal Cells

6.6 Ah cells with 8+ mAh/cm^2 cathode loading

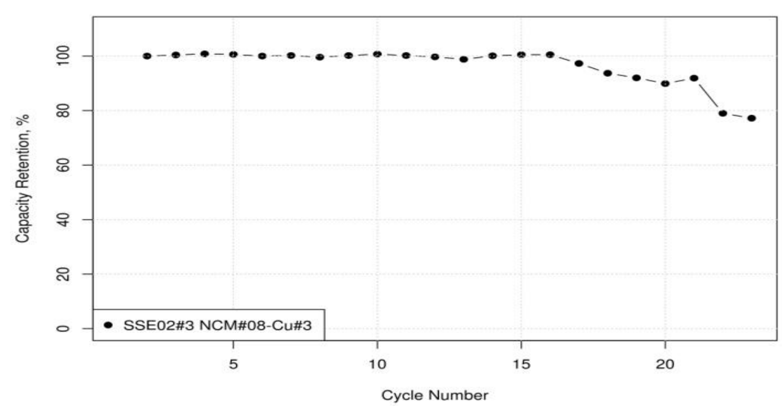




Cycle #	1
Cap., Ah	6.7
Cap., %	100
Cap., mAh/g(cathode)	189.1
Cap., mAh/g(active)	194.9
Cap., mAh/cm2	8.6
Eff., %	86.7
Mid Voltage, V	3.768
Energy, Wh	25.1
Energy, mWh/g(cell)	484.1

Cathode Loading: 45.5 mg/cm2

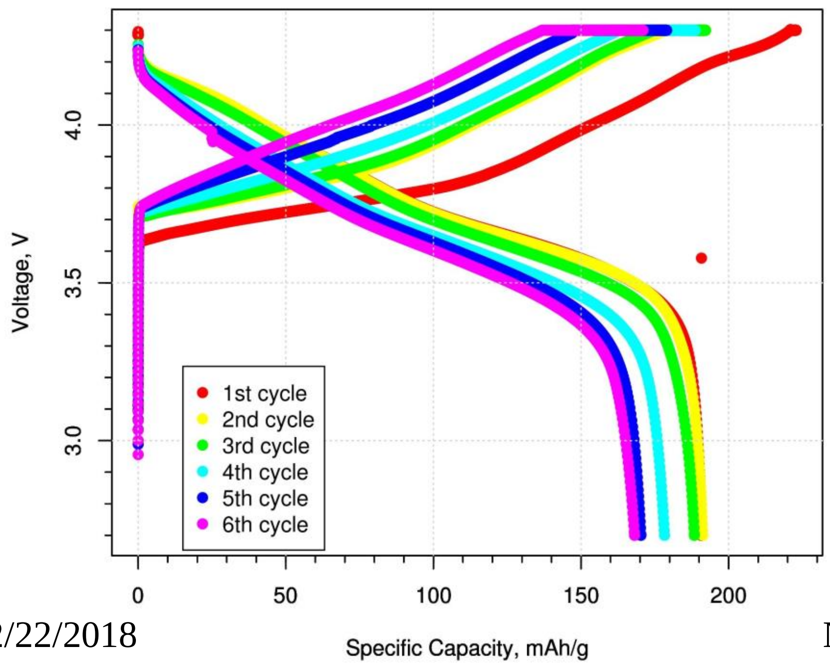
Cell Weight: 51.8 g

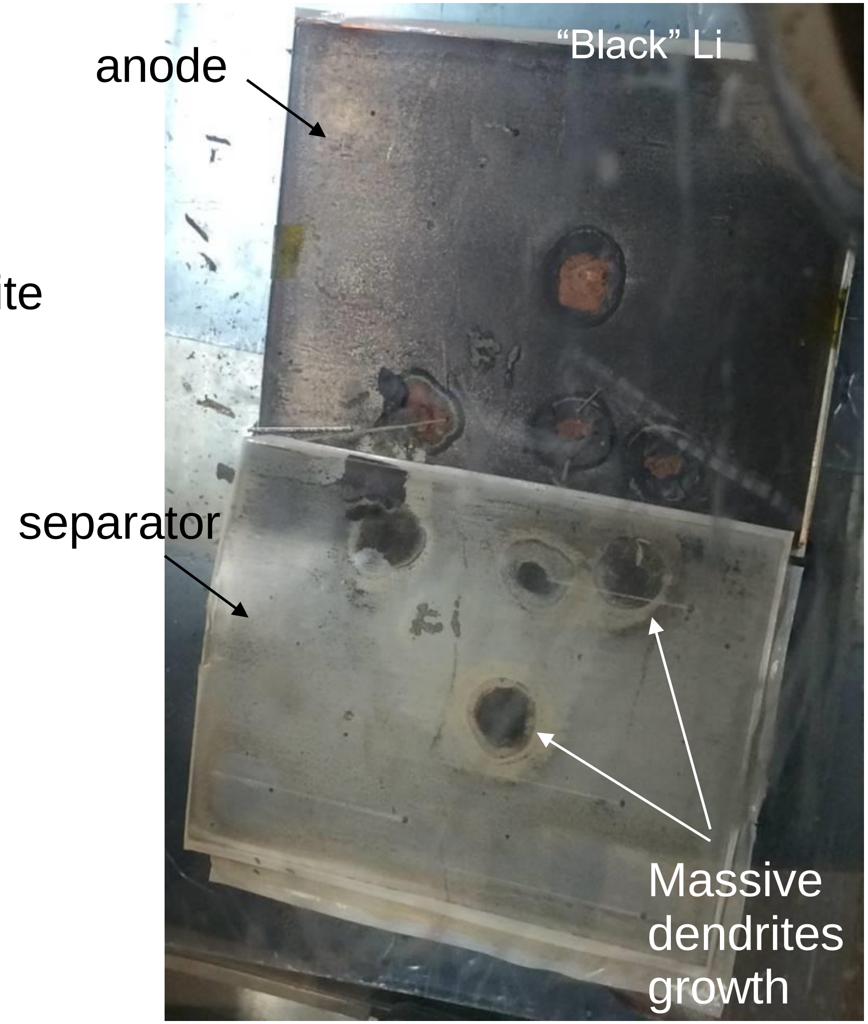


Problem:
Limited Cycle Life Performance

Anode failure as a primarily reason for cell degradation:

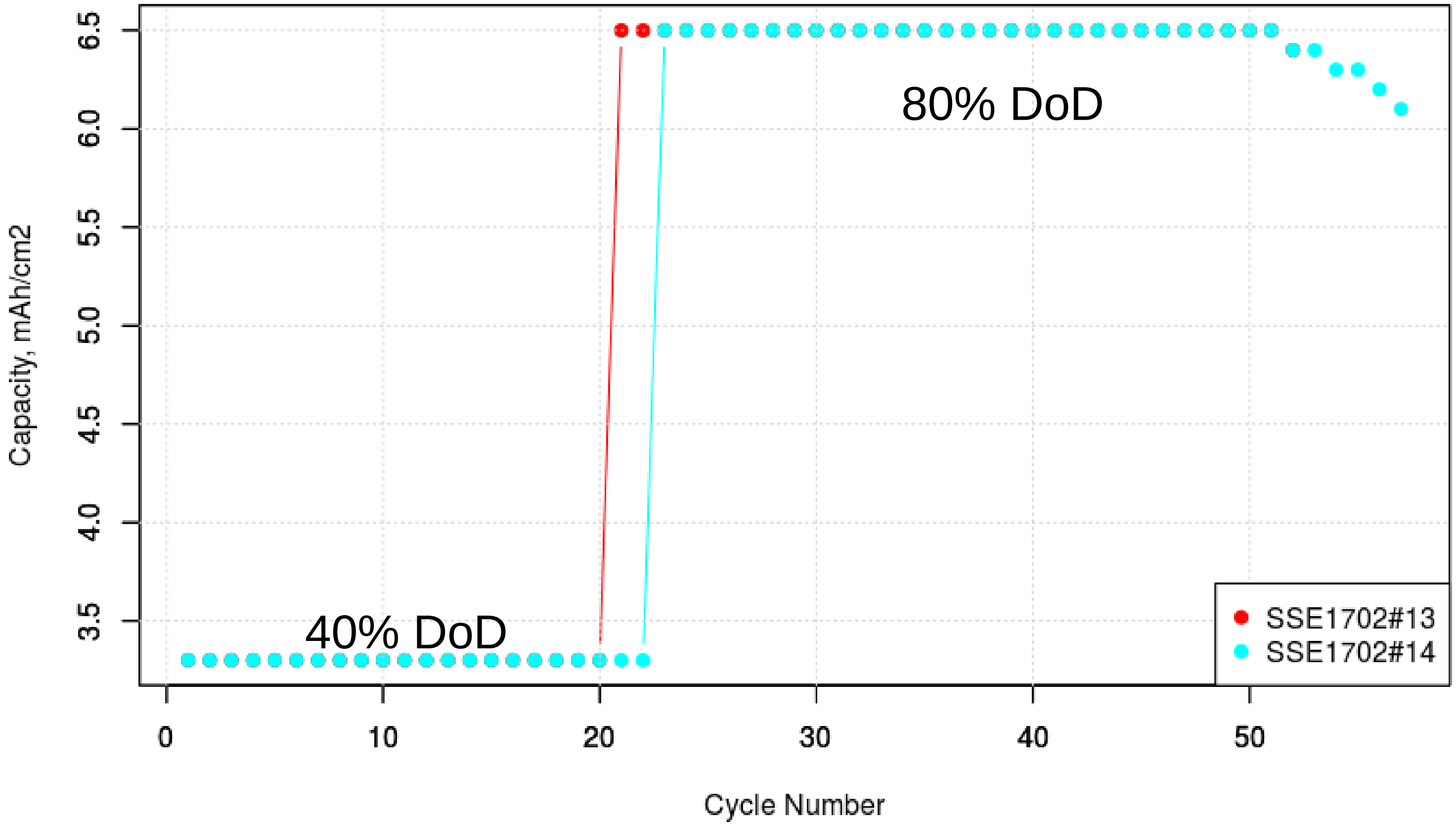
- Mossy lithium growth during charge
- Non-uniform Li stripping during discharge
- Copper roughness promotes lithium dendrite nucleation
- No barrier to dendrites growth



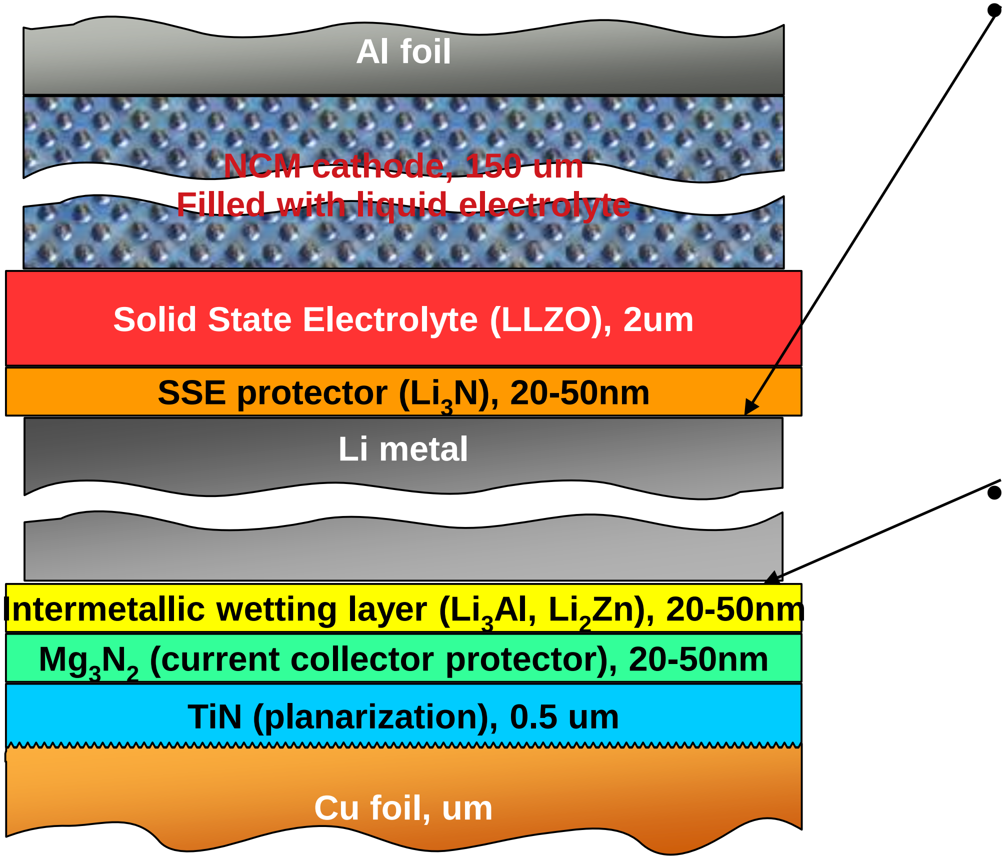


Solution #1: Cycling Protocol Optimization

- Slower charging (slower Li plating)
- Shallow discharge (less mobile Li)



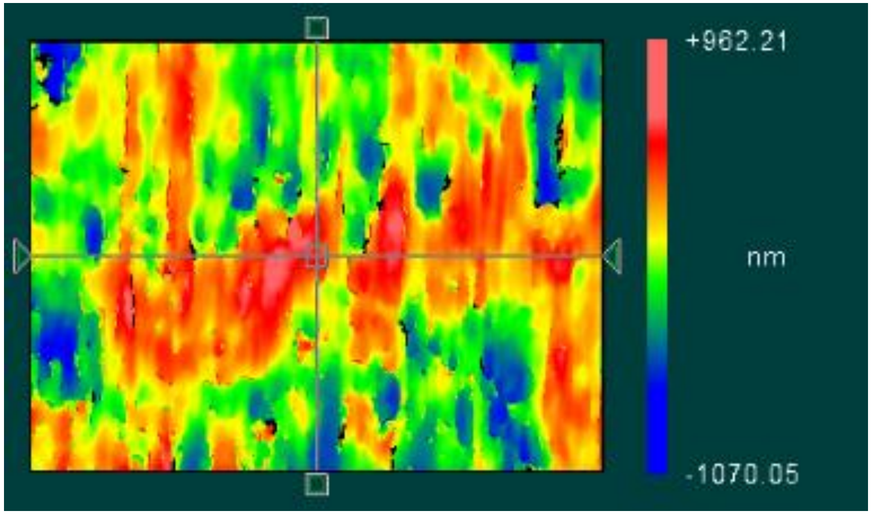
Solution #2: Lithium Interfaces Engineering

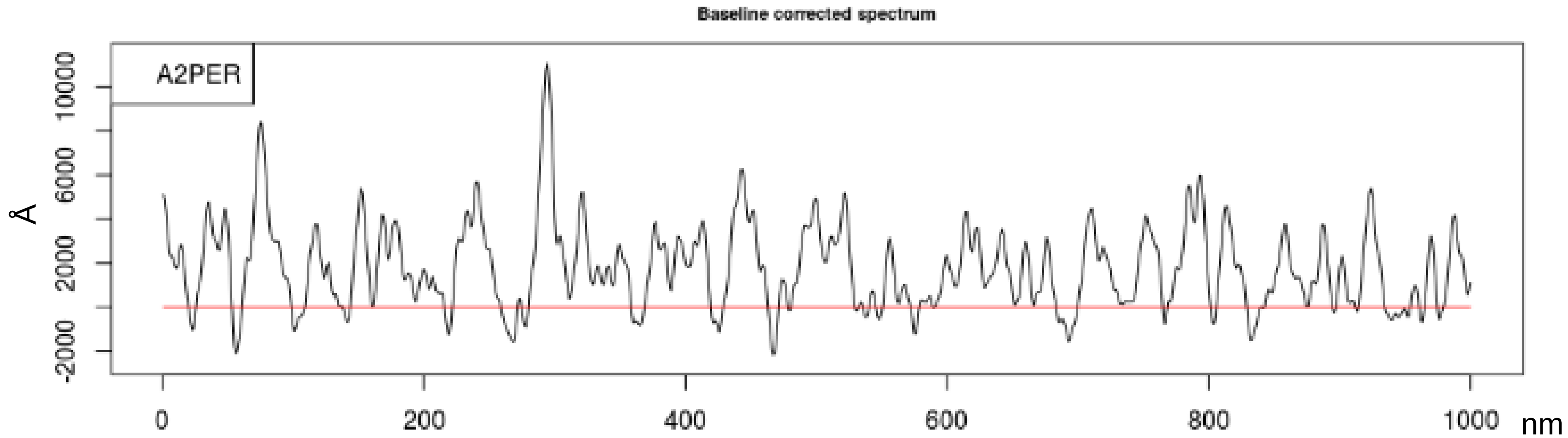


- Li metal facing anode
  - Dendrites growth blocking (hard, defect-free)
  - Thermodynamically stable chemistry
  - Must be good Li-ion conductor
- Li metal facing current collector
  - Dendrites seeding blocker (smooth, good wetting by Li)
  - Thermodynamically stable chemistry
  - Must be electronically conductive

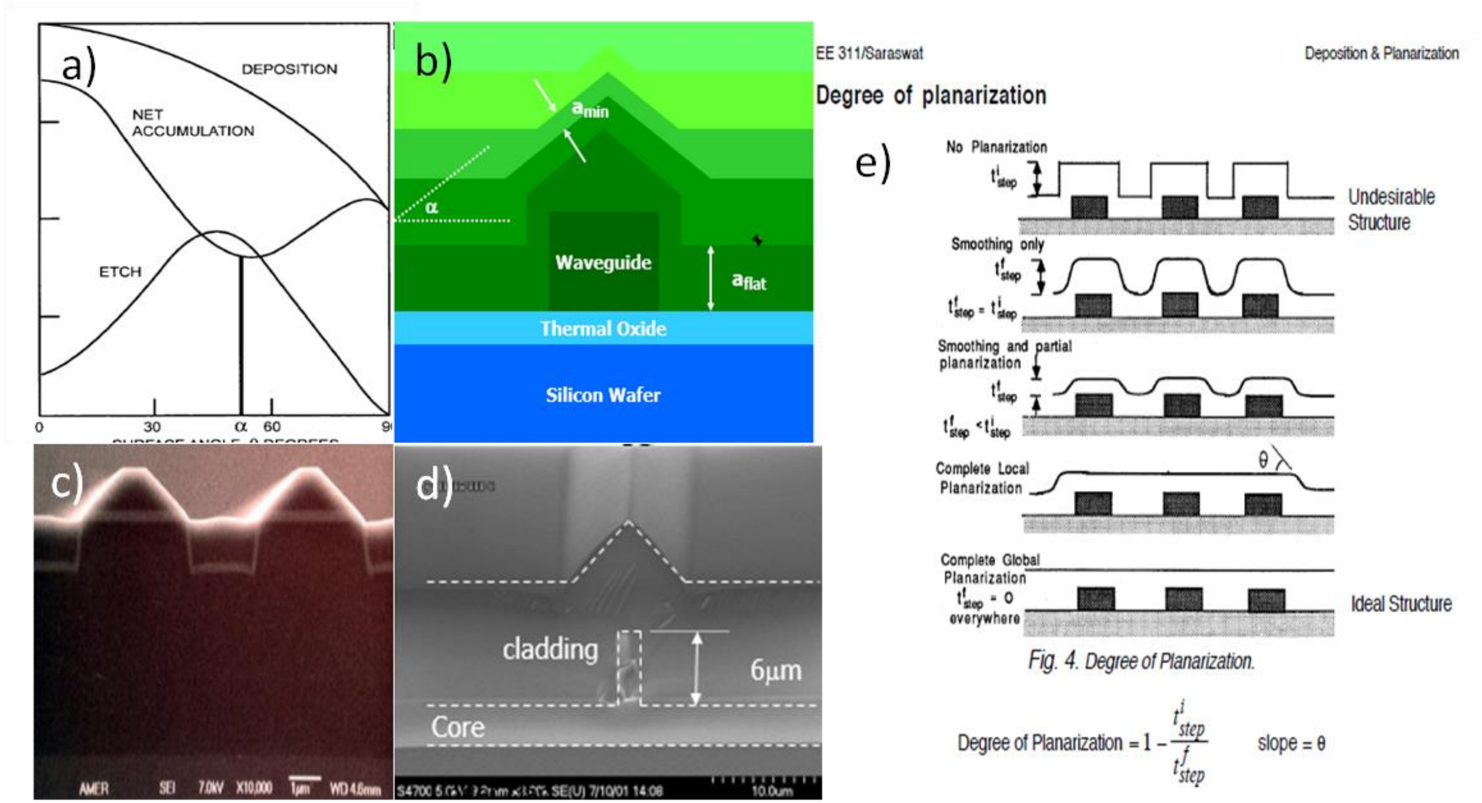
Copper Roughness and Impurities

- Copper foil roughness can seed Li dendrites rough
- 110 Copper is 99.9% pure copper – main impurity is oxygen (0.05% max)
- Planar and clean surface is required for reversible Li plating



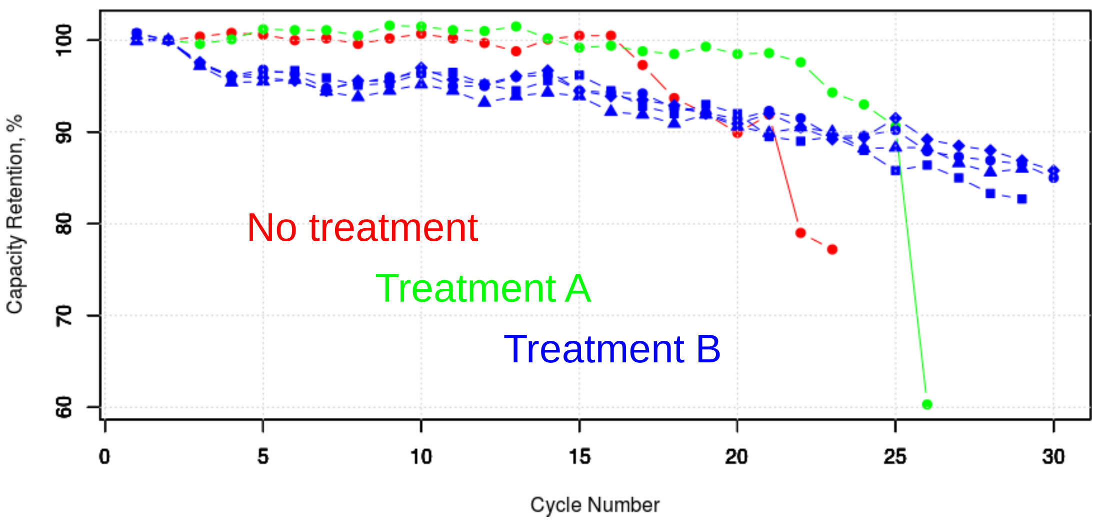


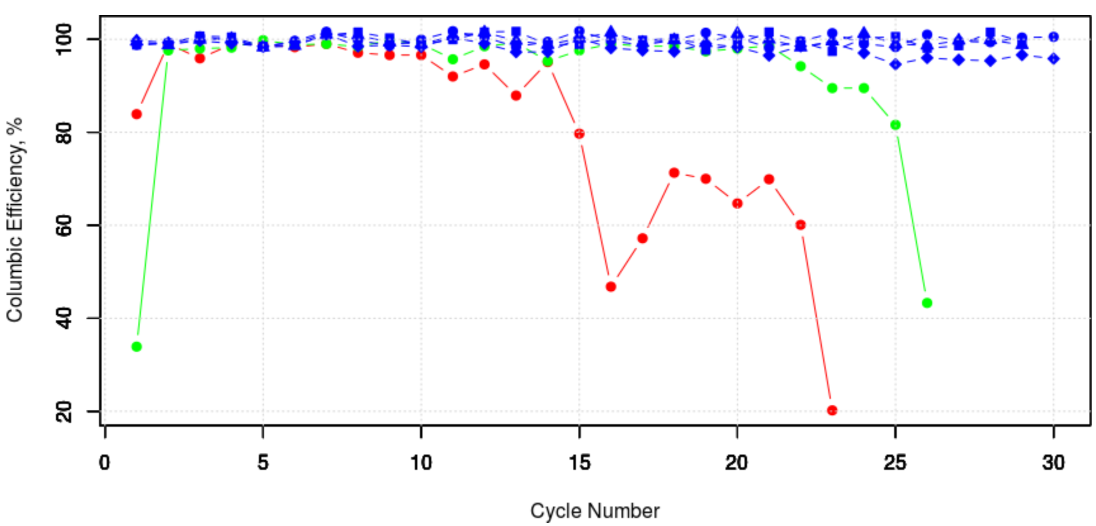
Planarization Layer



- Large area dielectric Films can be deposited and planarized at high speed by RF Biased DC Reactive Sputtering, Ion densifying and planarizing a dielectric film
- A thin (~0.2 um) Planarization Layer is deposited on the anode copper current collector and planarized to eliminate high spots where Li dendrites can form

Surface Preparation for Li Plating
Impact on Cell Cycling



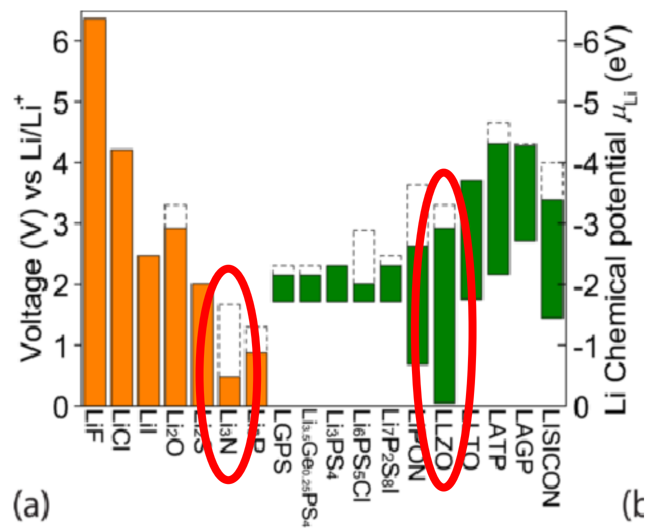


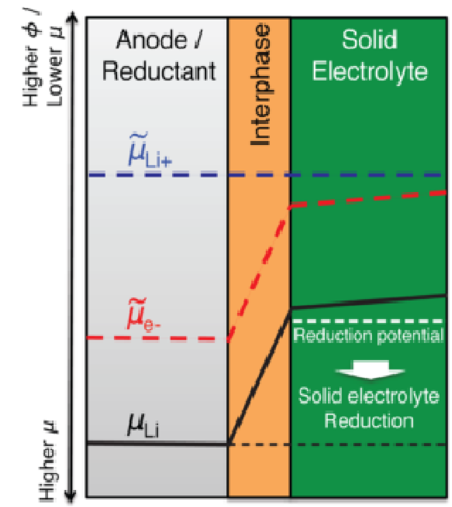
Li dendrites growing through separator

Cell post-mortem: separator

Solid State Electrolyte
Lithiation from Cathode inside Sealed Cell

- Dense glassy (defect-free) oxide layer deposited using RF-biased Pulsed DC Reactive Sputtering
- SSE of choice: Ga-substituted LLZO:
  - $5.4 \cdot 10^{-4}$ S/cm at 20 ºC
  - Lithiation from cathode developed by SPL allows:
    - Cell assembly in air with non-lithiated version (lithiated version is air sensitive);
    - High throughput reactive sputtering of oxide from intermetallic target
  - Interfacial Li_3N is formed during first lithiation from nitrogen-reach surface layer



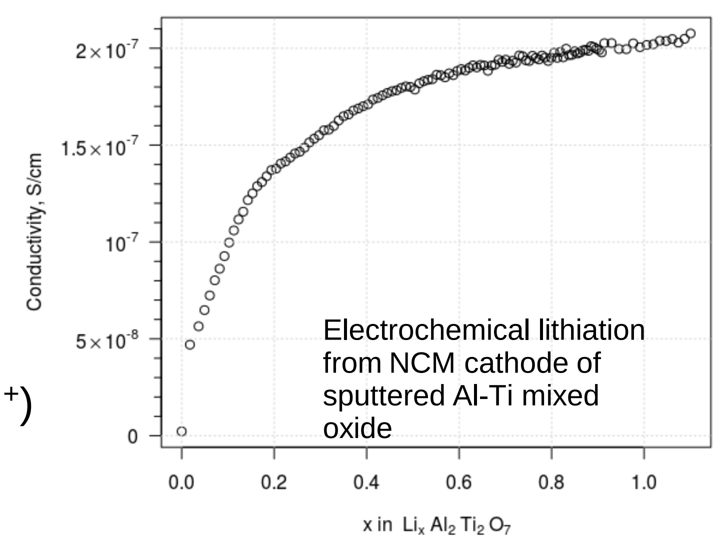


Reactive Sputtering:

$La_{(54.6\%)}Ga_{(15\%)}Zr_{(30.4\%)}$ intermetallic + $6O_2 = La_{6.55}Ga_{0.15}Zr_2O_{12}$

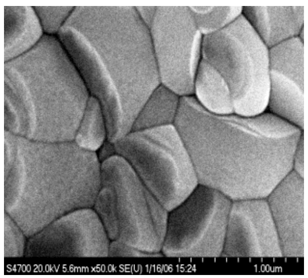
Electrochemical Lithiation:

$La_{6.55}Ga_{0.15}Zr_2O_{12} + 7Li = Li_7La_{6.55}Ga_{0.15}Zr_2O_{12}$ (E = 0V vs. Li/Li$^+$)



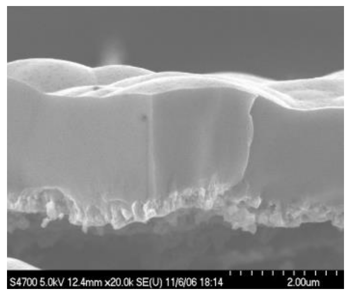
Long Cycle Life Li Metal Batteries
Solid-State Micro Batteries

- TF-SSE is proven in manufacturing to efficiently prevent growth of dendritic lithium
  - ST Micro warranties 5,000 cycles in their commercial small scale cells
  - Excellatron published data showing more than 50,000 cycles



Sputtered crystalline LiCoO2 cathode

+



Defect-free LIPON SS Electrolyte

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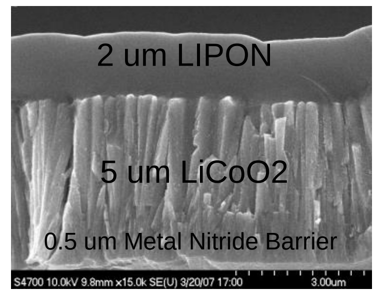

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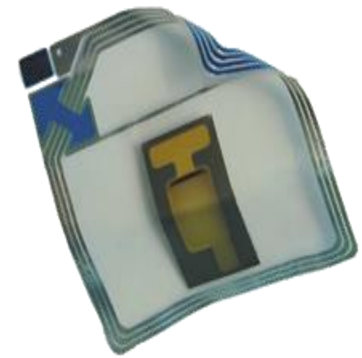
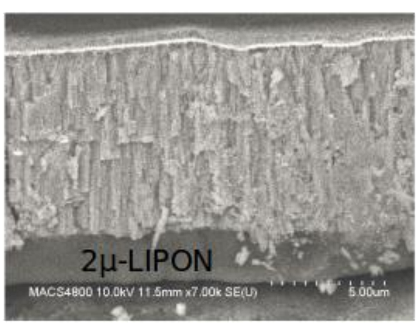
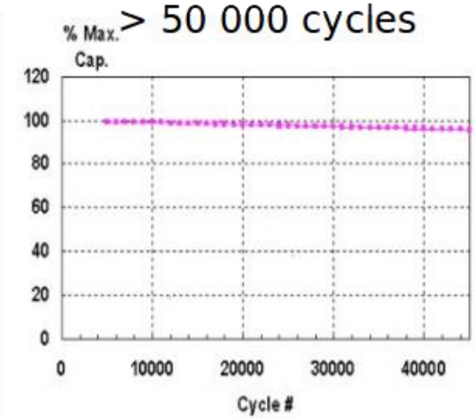


IPS "Thinergy" TFμB on Cu/Ni foil

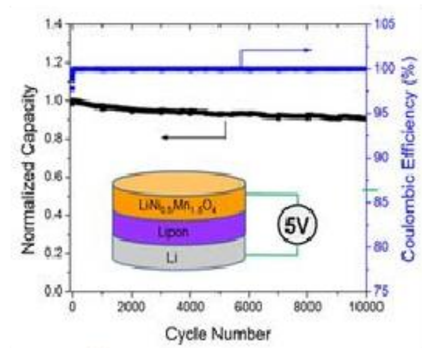
STMicro EnFilm™ Battery
4000 cycles



Excellatron data
> 50 000 cycles



ORNL data – N. Dudney, et. al.
> 10 000 cycles



http://ceramics.org/wp-content/uploads/2011/08/energy-ss-batteries-jones.pdf
Adv. Energy Mater. 2015, 5, 1401408

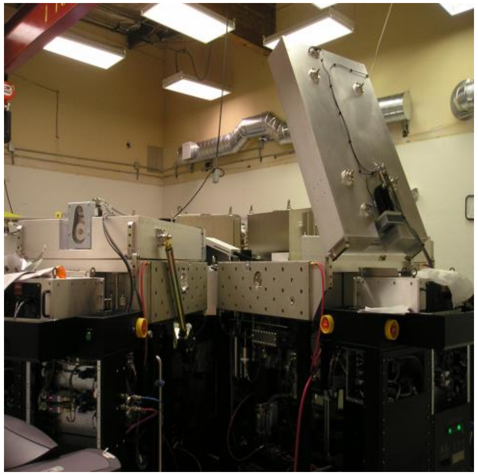
Manufacturability and Cost

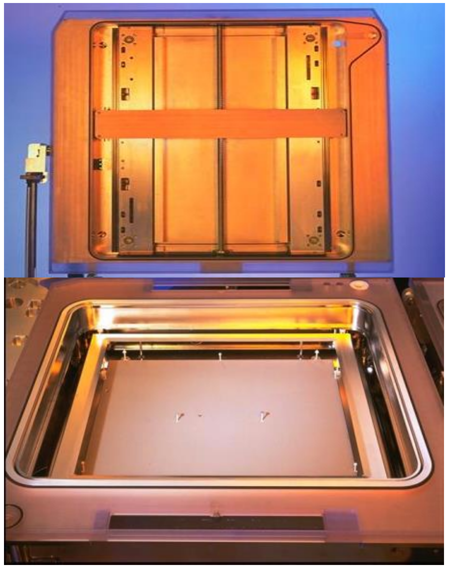
- **DLLC patents pioneer wide area reactive sputtering of optical and barrier films based on TFT-LCD flat panel display manufacture with high quality and low cost**

- **This same technology will be used in making the battery with sputtered layers affordable and manufacturable in volume**

cluster tool with 5 chambers for sputtering of layers without cross contamination;

RF biased Pulsed DC reactive sputtering, first unit: February 2005.





Sputtering equipment used for demonstration stage:
900 cm^2 chamber;
deposition rate 8-10 min/um (1 min/um in production)

Overview on Battery Chemistry

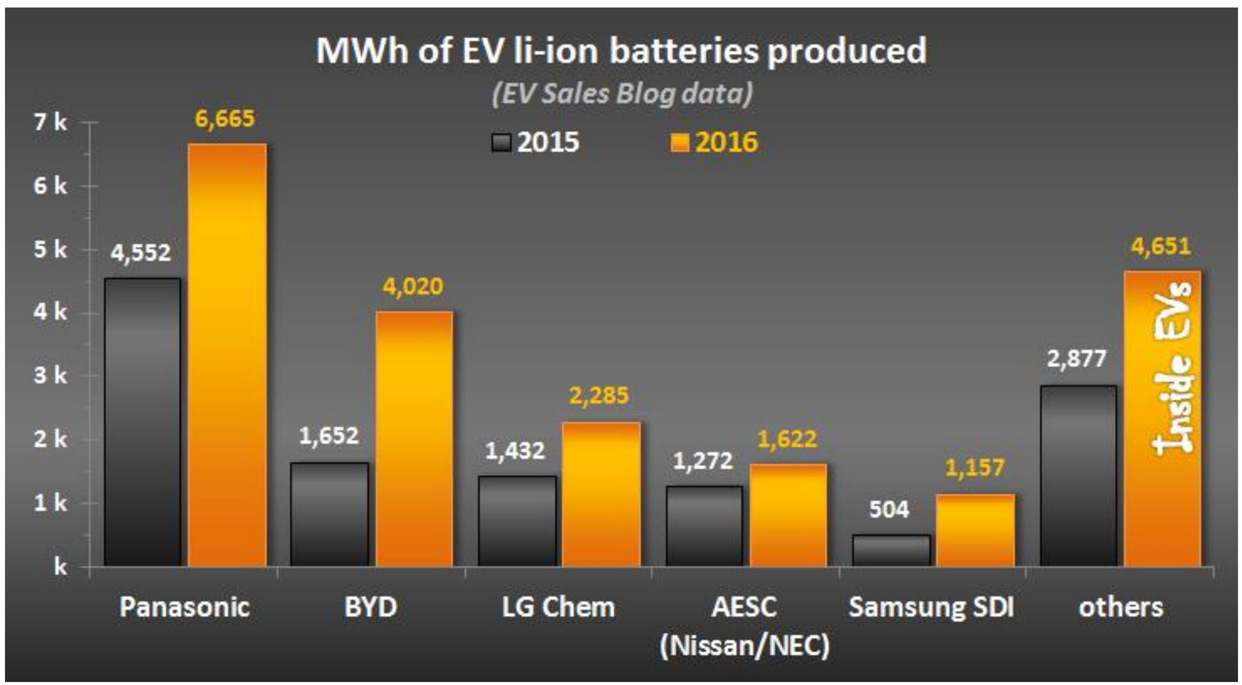
Specifications	Lead Acid	NiCd	NiMH	Li-ion		
				Cobalt	Manganese	Phosphate
Specific Energy Density(Wh/kg)	30-50	45-80	60-120	150-190	100-135	90-120
Internal Resistance (mΩ)	<100 12V pack	100-200 6V pack	200-300 6V pack	150-300 7.2V	25-75 per cell	25-50 per cell
Life Cycle (80% discharge)	200-300	1000	300-500	500-1,000	500-1,000	1,000-2,000
Fast-Charge Time	8-16h	1h typical	2-4h	2-4h	1h or less	1h or less
Overcharge Tolerance	High	Moderate	Low	Low. Cannot tolerate trickle charge		
Self-Discharge/month(room temp)	5%	20%	30%	<10%		
Cell Voltage (nominal)	2V	1.2V	1.2V	3.6V	3.8V	3.3V
Charge Cutoff Voltage(V/cell)	2.40 Float 2.25	Full charge detection by voltage signature		4.2		3.6
Discharge Cutoff Voltage(V/cell, 1C)	1.75	1		2.50-3.00		2.8
Peak Load Current Best Result	5C 0.2C	20C 1C	5C 0.5C	>3C <1C	>30C <10C	>30C <10C
Charge Temperature	-20 to 50°C -4 to 122°F	0 to 45°C 32 to 113°F		0 to 45°C 32 to 113°F		
Discharge Temperature	-20 to 50°C -4 to 122°F	-20 to 65°C -4 to 149°F		-20 to 60°C -4 to 140°F		
Maintenance Requirement	3-6 Months (topping charge)	30-60 days (discharge)	60-90 days (discharge)	Not required		
Safety Requirements	Thermally stable	Thermally stable, fuse protection common		Protection circuit mandatory		
In Use Since	Late 1800s	1950	1990	1991	1996	1999
Toxicity	Very High	Very High	Low	Low		

Lithium Ion Battery Technologies

Type	LTO or Li-titanate	LFP or Li-phosphate	LMO or Li-manganese (spinel structure)	Short form: LCO or Li-cobalt.	NMC (NCM, CMN, CNM, MNC, MCN similar with different metal combinations)	NCA or Li-aluminum
Date	Commercially available since about 2008.	Since 1996	Since 1996	Since 1991	Since 2008	Since 1999
Specific energy (capacity)	50–80Wh/kg	90–120Wh/kg	100–150Wh/kg	150–200Wh/kg. Specialty cells provide up to 240Wh/kg.	150–220Wh/kg	200-260Wh/kg; 300Wh/kg predictable
Cycle life	3,000–7,000	1000–2000 (related to depth of discharge, temperature)	300–700 (related to depth of discharge, temperature)	500–1000, related to depth of discharge, load, temperature	1000–2000 (related to depth of discharge, temperature)	500 (related to depth of discharge, temperature)
Applications	UPS, electric powertrain (Mitsubishi i-MiEV, Honda Fit EV), solar-powered street lighting	Portable and stationary needing high load currents and endurance	Power tools, medical devices, electric powertrains	Mobile phones, tablets, laptops, cameras	E-bikes, medical devices, EVs, industrial	Medical devices, industrial, electric powertrain (Tesla)
Comments	Long life, fast charge, wide temperature range but low specific energy and expensive. Among safest Li-ion batteries.	Very flat voltage discharge curve but low capacity. One of safest Li-ions. Used for special markets. Elevated self-discharge.	High power but less capacity; safer than Li-cobalt; commonly mixed with NMC to improve performance.	Very high specific energy, limited specific power. Cobalt is expensive. Serves as Energy Cell. Market share has stabilized.	Provides high capacity and high power. Serves as Hybrid Cell. Favorite chemistry for many uses; market share is increasing.	Shares similarities with Li-cobalt. Serves as Energy Cell.

Lithium Ion Battery Trends

In 2016, sales of LIBs for electric vehicles increased by some 66%, up from 12.3 GWh of capacity to 20.4 GWh. The pace of battery production growth is even faster than the growth of EVs themselves (up ~40% worldwide last year), as average battery capacity inside those sales is growing at the same time**.** LIBs are the go-to source for EV power right now. Many other products use LIBs: chainsaws, mini-cameras, solar window chargers, wheelchairs, bicycles, portable self-charging desks. The battery market is expected to exceed $33 billion by 2019 and $46 billion by 2023.



Early Target Markets

- **400+ Wh/kg / 50+ cycles** we can sell to DoD Aircraft/drones, Small Satellites, and portable power.
- **400+ Wh/kg / 100+ cycles** we can start selling to commercial applications.

Market Segments	Customers	Market Technology Need	Market Volume	Market Pricing
Space Launch and Satellites	DOD and Commercial	Safety, Durability, **High Energy Density**, High Charge/discharge rates, Long Cycle Life	Low	Very High
Implantable Devices	Commercial	Safety, Durability, **High Energy Density**	Medium	Very High
Missiles and RV	DOD	Safety, Durability, **High Energy Density**, High Charge/discharge rates	Low	High
Directed Energy Weapons	DOD	Safety, Durability, **High Energy Density**, High Charge/discharge rates	Low	High
Aircraft	DOD	Safety, Durability, **High Energy Density**, High Charge/discharge rates, Long Cycle Life	Low	High
	Commercial		Medium	High
Drones and UAS	DOD	Safety, Durability, **High Energy Density**, High Charge/discharge rates	Low	Medium
	Commercial		Low but Growing	Medium
Portable Power Devices	DOD	Safety and **High Energy Density**	Medium	Medium
	Medical		Large	Medium

News February 2018

Two examples of examples of emerging markets

Feb 15, 2018: SpaceX is about to quietly launch the first 2 of nearly 12,000 satellites to blanket Earth in high-speed internet. The scale of the proposal, informally known as Starlink, is incredible. In the coming years, the company hopes to launch 4,425 interlinked broadband-internet satellites into orbit some 700 to 800 miles above Earth, plus another 7,500 spacecraft into lower orbits.

Launch costs are ~$2,500 per Lb, and ~20% of satellite weight is its battery pack module. Going from 200 to 500 wh/kg saves ~60% launch cost.

Feb 17, 2018: Lilium is developing a five-seat electric aircraft that can take off and land vertically. The plane, which is capable of flying for up to an hour on the single charge, will also be able to take short trips between cities. According to the company's website, the jet will be able to travel over 40 miles in around 15 minutes. The jet's total range will be around 190 miles, making it possible to travel between Boston and New York City in about an hour.

Summary

- SpectraPower previously demonstrated Lithium cells with capacities of up to 500 Whr/kg, but with limited cycle life
- Since then, SpectraPower has formed a collaboration with Demaray LLC to scale technologies used in small (<1mAh), solid state Lithium cells which have demonstrated many 1,000s of cycles
- These small solid-state Lithium cells are in large scale commercial production today using processes invented by Dr. Ernest Demaray
- Dr. Demaray previously scaled his RF-biased DC pulsed sputtering for large scale applications such as flat screen TVs and window coatings
- SpectraPower and Demaray have designed a Lithium cell using large scale sputtering technology with SpectraPower's cathode. Technology development is in progress.
- Patent application "Thin film Battery with High Capacity, energy Density and Cycle life"US20180006293A1